

On-Shore Production of Crude Oil and Natural Gas

Sulfur Plants

Emission Test Report Getty Oil Company New Hope, Texas EMISSION TEST REPORT

SO₂ TESTING

AT THE

GETTY OIL NEW HOPE PLANT

NEW HOPE, TEXAS

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INTRODUCTION

This report presents the results of testing for sulfur dioxide, reduced sulfur, and nitrogen oxide emissions from the Claus incinerator stack at the Getty Oil New Hope Plant, near Mt. Pleasant, Texas. The testing was performed by Radian Corporation on April 6 through April 13, 1981. This work was funded and administered by the Emission Measurement Branch of the U. S. Environmental Protection Agency. The results of this testing will be used to develop New Source Performance Standards for on-shore production facilities.

The following sections present a summary of results, a description of the process configuration, location of sampling points, the testing methodology, quality assurance/quality control procedures, and complete results and example calculations. A full listing of the data and other supplemental information are included as appendices.

SUMMARY OF RESULTS

This section presents a summary of the testing data at the Getty Oil New Hope Plant. The complete test results and example calculations are presented in Section 7. All of the supporting data sheets are included in Appendix A.

The results for the SO_2 , H_2S , and TRS tests are summarized in Table 2-1. This table also presents the liquid sulfur production data, the calculated sulfur emission rate (SO_2 plus TRS), and sulfur recovery efficiencies. Figure 2-1 graphically presents on a daily basis the sulfur recovery efficiency, the SO_2 emission rate, and the liquid sulfur production.

TABLE 2-1. SUMMARY OF RESULTS - GETTY OIL, NEW HOPE

SO ₂ (ppm)			H ₂ S	(ppm)	TRS	SO ₂ aOut	Sulfur(s) b Out	Liquid Sulfur	Plant %
Date	Range	Average	Range	Average	(ppm)	Stack (lb/hr)	Stack (LTPD)	Make (LTPD)	Efficiency
4/8	8,300-9,840	8,950	426-662	545	1,050	1,318	7.1	144.7	95.3
4/9	8,950-13,600	10,520	446-925	637	1,460	1,565	8.4	146.2	94.6
4/10	9,360-10,300	9,950	333-1,800	959	977	1,181	6.3	123.2	95.1
4/11	8,930-9,370	9,080	331-402	359	657	1,116	6.0	113.0	95.0
4/12	8,850-9,480	9,150	144-408	244	787	1,141	6.1	113.0	94.9
TEST									
	8,300-13,600	9,517	144-1,800	549	972	1,264	6,8	128.0	95.0

a Includes SO₂ plus TRS expressed as SO₂ b Includes SO₂ plus TRS expressed as S

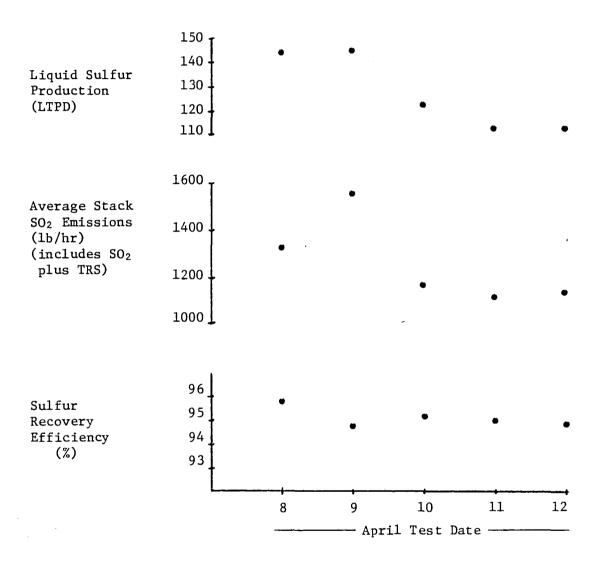


Figure 2-1. Summary of SO_2 emissions and sulfur recovery at Getty Oil's New Hope Plant.

PROCESS DESCRIPTION

The Getty Oil New Hope Plant is a gas processing facility that combines natural gas liquids removal and gas sweetening. The feed gas to the plant is from area gas wells. The natural gas liquids are removed, then the natural gas is sweetened using an amine scrubbing unit. Sulfur is recovered using a Claus sulfur plant. The natural gas processed is higher in H₂S than CO₂ and the acid gas feed to the Claus plant is relatively high in H₂S content (about 55 volume percent during the test period). The design capacity of the plant is 60 MMSCFD of gas and the plant was treating approximately 27 MMSCFD of gas during the test period. The Claus plant has a capacity of about 150 long tons per day (LTPD) of liquid sulfur and was producing between 110 and 150 LTPD during the test period.

A simplified schematic of the process is shown in Figure 3-1. The raw gas stream is first treated to remove and recover the natural gas liquids which are present. The acid gases in the gas stream are then removed by an ethanolamine scrubbing unit. The hydrogen sulfide (H_2S) released during regeneration of the scrubbing liquor is processed in a Claus sulfur plant to recover elemental sulfur. The Claus plant is a dual-train three-stage catalytic unit, with the third catalytic reactor being common to both trains. Liquid sulfur from the Claus plant is collected in a below-ground storage tank and sold. The acid gases remaining in the Claus plant tail gas are routed to an incinerator to convert the H_2S to SO_2 prior to emission to the atmosphere.

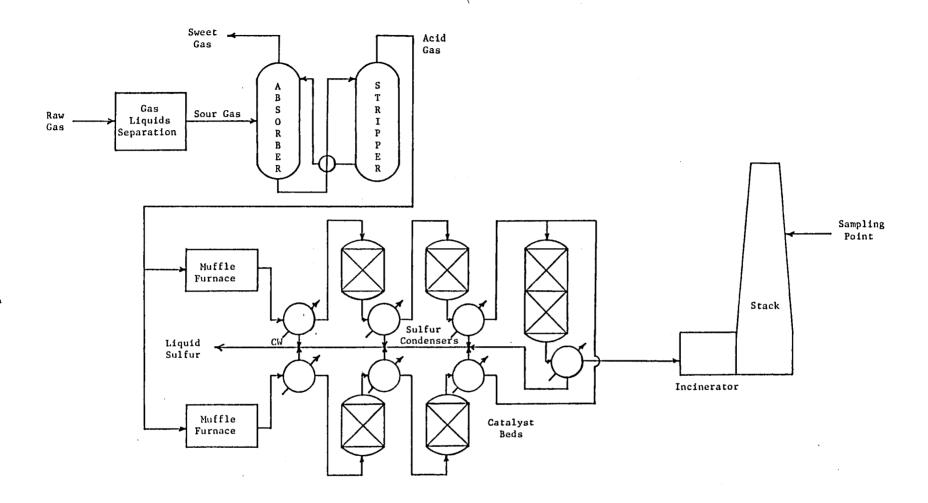


Figure 3-1. Simplified flow diagram.

Testing of the Claus plant incinerator stack was performed to determine the level of sulfur emissions, SO_2 , H_2S , and total reduced sulfur (TRS), in the stack. In addition, the liquid sulfur production was monitored to allow estimation of the efficiency of the sulfur recovery plant.

LOCATION OF SAMPLING POINTS

Gas-phase samples were collected on the incinerator stack that services the off-gases from the Claus unit. Sampling was performed on the 180° sampling platform located approximately 70 feet off the ground. Two three (3") inch ports were available for sampling. The location and orientation of these ports are shown in Figure 4-1.

Only two ports were required to perform a velocity traverse due to the relatively small stack diameter (4.08 ft). A six-point traverse of each diagonal was performed. The distances into the stack for point 1 is 2.2 inches; point 2, 7.2 inches; point 3, 14.5 inches; point 4, 34.5 inches; point 5, 41.8 inches; and point 6, 46.8 inches. The proposed three-point sampling technique used to collect the various gas-phase samples was eliminated in favor of a single-point of average velocity. Since the sampling points are located greater than eight stack diameters from the nearest upstream or downstream disturbance and the velocity profile was relatively constant across each diagonal, the gas stream should be homogenous at the sampling points. Figure 4-2 shows the location of the sampling points with respect to upstream and downstream stack disturbances.

All of the gas samples were collected through the W port. Samples were collected at both point W2, which is 7.2 inches into the stack, and W4, which is 34.5 inches into the stack. The field data sheets in Appendix A indicate which point was used for each sample.

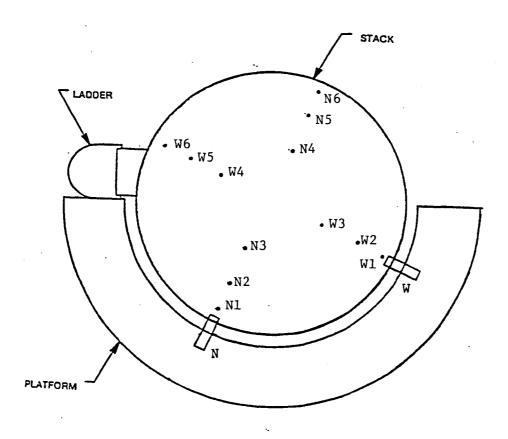


Figure 4-1. Location of sampling ports and velocity traverse points

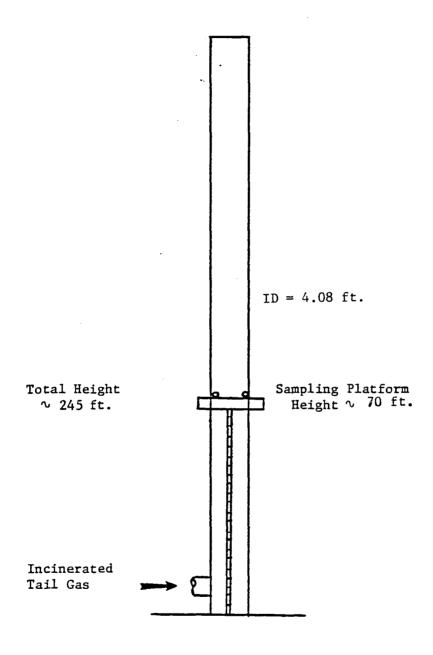


Figure 4-2. Location of upstream and downstream disturbances from sampling ports.

SAMPLING AND ANALYTICAL METHODOLOGY

To meet the objectives of this project, the following gas-phase parameters were measured at the incinerator stack sampling platform:

- · volumetric gas flow rate,
- molecular weight,
- moisture content,
- · SO₂,
- NO_×,
- H₂S, and
- total reduced sulfur (TRS).

In addition to the above parameters, the liquid sulfur production rate was also monitored. Whenever possible, referenced source sampling and analysis methods were used during testing at the New Hope Plant. Table 5-1 lists the various parameters measured and the sampling and analysis methods used to monitor these parameters. A description of the sampling and analytical methodology is provided in Appendix B.

TABLE 5-1. SAMPLING/ANALYSIS PARAMETERS AND METHODOLOGY

Parameter to be Measured	Methodology
Volumetric Gas Flow Rate	EPA Method 2
Gas-Phase Molecular Weight	EPA Method 3
Gas-Phase H ₂ O	EPA Method 4
Gas-Phase SO ₂	EPA Method 6
Gas-Phase NO _×	EPA Method 7
Gas Phase H ₂ Ŝ	EPA Method 11
Gas-Phase TRS	EPA Method 16A
Liquid Sulfur Production	No Reference Method

The moisture content of the incinerator flue gas at the New Hope Plant was determined using the methodology specified in EPA - Method 4. Attempts were made early in the sampling program at the Warren Petroleum - Monument Plant to collect both SO2 and moisture samples with the same sampling train (EPA Method 6). By weighing the impingers before and after sampling the mass of water collected during sampling could then be related to the moisture content of the gas. But, because the gas volume collected during SO2 sampling was only 20 to 30 liters, the total mass of water collected during sampling was 2.5 to 4.0 grams based on 15% $\rm{H}_{2}O$ in the gas. Small losses ($\rm{^{\circ}}1.0$ grams) in the recovery of the collected H_2O could have a large effect in the apparent moisture content of the gas. To alleviate this problem, a separate sampling train (EPA Method 4) was set up by using larger impingers at a higher gas flow rate to collect the H2O samples. This sampling arrangement allowed a larger volume of gas ($^{\circ}$ 150 liters) and a larger mass of water (15 to 20 grams) to be collected. Small losses in the recovery of the collected water did not have as significant effect on the moisture determination.

The proposed three-point traversing technique used to collect the various gas-phase samples was eliminated during this testing period. Instead, a single point of average velocity was used to collect a majority of the gas-phase samples. The decision to eliminate the three-point traverses was based upon two facts. First, the sampling ports are situated approximately ten stack diameters upstream from the nearest disturbance. Second, the velocity profile is relatively consistent across each diagonal. To help insure that the gas sample was homogenous by the time it reached the sampling ports, four sets of gas samples were collected at a separate point within the stack. Analysis of these gas samples for SO_2 , H_2S , O_2 , CO_2 , and N_2 indicated that the concentration of these constituents were the same (within experimental error) at both points in the stack.

Because of the very low particulate concentration in the incinerator gas, a decision was made to eliminate the glass wool plug from the probe liner. This decision eliminated the systematic placement and removal of a

glass wool plug from a 850°F probe in-between SO_2 and H_2S sample collection runs. The glass plug is designed to remove particulate from the gas-phase during SO_2 (EPA Method 6) and NO_{\times} (EPA Method 7) sample collection. However, during H_2S (EPA Method 11) and TRS (EPA Method 16A) sampling, the glass wool plug is eliminated to minimize sorption losses of these gas species across a particulate cake. By eliminating the glass wool plug, the probe did not have to be removed from the stack in-between each sample. This minimized the time that the extremely hot (850°F) probe had to be handled resulting in increased personnel safety with a minimum of down time in-between runs.

QUALITY ASSURANCE/QUALITY CONTROL

A comprehensive quality assurance/quality control (QA/QC) program (Radian DCN 81-222-018-04-09) was designed and implemented during this program. The objective of this QA/QC program was to assess and document the precision, accuracy, and adequacy of emission data developed during sampling and analysis.

A summary of the QA/QC results obtained during activities at the Good Hope Plant are presented in this section. A brief discussion of the precision, accuracy, and data capture are also presented in this section of the report. Copies of the equipment calibration forms and reagent preparation/standardization forms are presented in Appendix B.

ASSESSMENT OF DATA QUALITY

Table 6-1 summarizes the estimated and measured precision, accuracy, and data capture for each of the parameters monitored at the Good Hope Plant. The measured precision and accuracy for each of the parameters fall within the original estimates. Deviations from estimated data capture are discussed later in this section.

DISCUSSION OF QA/QC RESULTS

During this project, the precision and accuracy of a particular measurement was determined by one or more of the following methods:

- performance audit,
- system audit, and
- quality control procedures.

Precision is defined here as a measure of mutual agreement among individual measurements of the same property. Precision can be qualified with respect to the replicability and repeatability of a particular parameter. Replicability is a measure of variability between measurements of the same parameter by the same analyst using the same apparatus on the same day and in the same laboratory. Routine duplicate analyses were used to measure replicability during the course of the project.

Repeatability is similar to replicability but requires that one or more of the following be different:

- analyst,
- · apparatus, or
- · the day.

Daily analysis of quality control standards by different analysts provided a measure of repeatability.

Accuracy is defined here as the degree of agreement of a measurement (or average of measurements of the same sample) with an accepted reference or true value. The accuracy data presented in Table 6-1 represents the relative accuracy of the measured value, X, with respect to the reference value, T, of a field audit sample. Results obtained during the field performance audit at the Monument Plant were also used to determine the accuracy of the data collected at the New Hope Plant.

TABLE 6-1. SUMMARY OF ESTIMATED AND MEASURED PRECISION, ACCURACY, AND DATA CAPTURE FOR THE DATA COLLECTED AT THE NEW HOPE PLANT

		Precision Meas	ured		1			
Measurement Parameter (Method)	Estimated (RSD)	Replicability (RSD)	Repeatability (RSD)	Accur Estimated ²	Measured	Data Ca Estimated	Measured ³	
Volumetric Gas Flow Rate (EPA 1 and 2)	20%	20% 4	20% 4	± 11%	± 11% 4	90%	100%	
Molecular Weight (Gas Partitioner)	10%	<2%	<2%	± 25%	<± 10%	90%	100%	
H ₂ O (EPA 4)	11%	11%*	11%4	± 10%	± 10% 4	90%	93%	
SO ₂ (EPA 6)	10%	0.31%	0.76%/1.2%5	± 20%	<±0.5%	90%	100%	
NO (EPA 7)	10%	6	6	± 20%	<±2.5%	90%	100%	
H ₂ S (EPA 11)	10%	N/A ⁷	N/A ⁷	± 20%	N/A 7	90%	100%	
Total Reduced Sulfur (EPA 16A)	51%	0.31%	0.76%/1.2%5	± 15%	<±0.5%	90%	100%	
Liquid Sulfur Production	10%			± 5%		100%	100%	

¹ Accuracy is based upon QA/QC Field Audit Performed at Monument Plant.

²Expected range for bias of method.

³The valid data percentage of the total tests required in the scope of work.

The Monument Plant field performance audit showed no deviation from accepted procedure. Precision and accuracy should be within the estimated values.

⁵Two different QC standards were used during the six day period. The 0.76% value is the mean RSD for analysis of the first standard over a four day period. The 1.2% value is the RSD for the second standard analyzed the last two days.

⁶NO precision cannot be properly calculated when all values are below the limit of quantitation (LOQ).

Refer to the text.

RSD = Relative Standard Deviation

RSD = Mean Relative Standard Deviation

All definitions and procedures used in calculating precision and accuracy were taken from Appendices A and C of the EPA document 600/9-76-005, Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I, Principles (1).

Data capture can be calculated by several different techniques. The data capture reported in Table 6-1 represents the valid data percentage of the total tests required in the scope of work.

The following list summarizes the deviations, exceptions, and special cases with respect to the precision, accuracy, and data capture data presented in Table 6-1. These include:

- The titrations of the peroxide impinger in the H_2S trains are included in the data base used in calculating precision for SO_2 analyses.
- The precision and accuracy reported for the TRS analyses is based on data from the SO_2 analyses since the analytical procedure (BaCl₂ titration, thorin indicator) is the same and comparable titrant volumes were used.
- Because of the lack of a suitably stable sulfide standard, no sulfide QC standard was analyzed. Precision data for H₂S analysis is not presented because duplicate analysis were not performed. The referenced analytical procedure requires that the whole sample be titrated, precluding duplicate analysis.
- Accuracy data for H_2S analysis are not presented. A "certified standard" bottle of H_2S gas is on order and will be used to determine the accuracy of the methodology.
- NO precision cannot be properly calculated when all values are below the "Limit of Quantitation" (LOQ).
- The reported accuracy data for molecular weight, SO_2 , NO_{\times} , and TRS reflect only the analytical phase of the measurement, as discussed in Sections 3.2.8, 3.5.8, and 3.6.8 of EPA document 600/4-77-027b (2). The performance audit activities address the sampling procedures.

- Both the precision and accuracy of the flue gas flow rate and moisture determination are based upon the performance audit performed at the Monument Plant. Since the field performance audit showed no deviation from accepted procedure, both the precision and accuracy are expected to lie within the estimated values. Further information concerning the field systems audit will be discussed in the separate QA/QC report.
- Results obtained from the second moisture run performed on April 10, 1981, appeared relatively high. Examination of the impinger weight gains showed that the second impinger registered an abnormally high weight gain. This data point has been classified as an outlier by means of the Dixon Criteria.

COMPLETE RESULTS AND EXAMPLE CALCULATIONS

This section presents the complete results and example calculations for testing performed at the Getty Oil New Hope Plant. All of the supporting data sheets are included as Appendix A.

The results for the velocity, gas composition, and SO_2 tests are shown in Table 7-1. This table also presents the calculated flow rates and SO_2 emission rates. Table 7-2 presents the test results for H_2S , TRS, and NO_{\downarrow} along with the calculated emission rates.

This section also presents example calculations which show how the test results were used to obtain flow rates, emission rates, and sulfur plant efficiencies.

TABLE 7-1. COMPLETE RESULTS: SO2, FLOW - GETTY OIL

GETTY DATE	OIL, RUN	NEW HOPE	02	CO2	N ₂	STACK TEMP(°F)	STACK PRESS("Hg)	%H ₂ O	VELOCITY (FT/S)	FLOW (ACFM)	FLOW (DSCFM)b	SO ₂ (ppm,dry)	SO ₂ (1b/hr)
4/8	1 2 3 AVG	0822 1107 1450	5.6 4.9 5.8 5.4	15.7 16.8 16.2 16.2	75.8 75.3 74.9 75.3	870 843 <u>823</u> 845	29.95 29.95 29.95 29.95	26.30 26.70 26.70 26.60	58.2 56.5 54.7 56.5	45700 44300 <u>42900</u> 44300	13200 13000 12800 13000	9840 8300 8700 8950	1310 1090 <u>1130</u> 1180
4/9	1 2 3 AVG	0815 1030 1645	5.2 5.6 3.5 4.8	16.6 16.2 17.9 16.9	75.5 75.7 75.7 75.6	861 855 <u>841</u> 852	29.92 29.92 29.92 29.92	26.10 27.00 29.30 27.50	58.9 58.3 55.5 57.6	46200 45700 <u>43600</u> 45200	13400 13200 12300 13000	8950 9010 13600 10520	1220 1210 1690 1370
4/10	1 2 3 AVG	0820 1020 1310	2.1 2.4 4.6 3.0	$ \begin{array}{r} 20.4 \\ 19.8 \\ \hline 17.5 \\ \hline 19.2 \end{array} $	74.1 74.3 74.7 74.3	791 760 <u>818</u> 790	30.12 $ 30.12 $ $ 30.12 $ $ 30.12$	$ 31.00 \\ 31.00 \\ \underline{26.90} \\ 29.60 $	45.5 44.3 49.4 46.4	35700 34700 38800 36400	10300 10300 <u>11600</u> 10700	10300 10200 <u>9360</u> 9950	1070 1060 <u>1100</u> 1080
20 4/11	1 2 3 AVG	0817 1011 1340	5.1 5.3 5.4 5.3	17.4 17.3 17.2 17.3	74.1 74.5 74.5 74.3	895 892 <u>897</u> 895	30.03 30.03 30.03 30.03	25.90 26.70 26.20 26.30	50.5 50.9 51.7 51.0	39600 39900 <u>40600</u> 40000	11300 11300 11500 11400	8930 8930 <u>9370</u> 9080	1020 1020 <u>1090</u> 1040
4/12	1 2 3 AVG	0807 1000 1240	5.6 5.4 5.2 5.4	17.2 16.9 17.3 17.1	74.1 74.5 74.7 74.3	880 893 898 890	29.99 29.99 29.99 29.99	27.00 26.60 27.10 26.90	50.8 51.3 51.9 51.3	39800 40300 40700 40300	11300 11400 11400 11400	8850 9480 <u>9120</u> 9150	1010 1090 1050 1050

FOOTNOTES:

a - Time reported is when velocity profile was begun.
 b - DSCFM at 60°F and 14.7 psia

TABLE 7-2. COMPLETE RESULTS: REDUCED SULFUR, NO, - GETTY OIL

GETTY OIL, NEW HOPE a		FLOW	H ₂	s^{b}	TRS		NO× ^c		
DATE	RUN	TIME a	(DSCFM)	Conc,ppm	1b/hr	Conc,ppm	lb/hr	Conc,ppm	lb/hr
4/8	1	0822	13200	426	57			13.0,	
	2	1107	13000	548	72	1050	138	<3.0 ^d	
	3	1450	12800	<u>662</u> 545	<u>86</u> 72			<3.0 <6.3	
	AVG		13000	545	72	1050	138	<6.3	<0.6
4/9	1	0815	13400	489	66			13.0	
	2	1030	13200	925	124	1460	195	<3.0	
	3	1645	<u> 12300</u>	<u>689,446</u>	<u>71</u> 87			$\frac{< 3.0}{< 6.3}$	
	AVG		13000	637	87	1460	195	<6.3	<0.6
4/10	1	0820	10300	1800	188			<3.0	
	2	1020	10300	745	77	977	101	<3.0	
	3	1310	11600	_333	39		-	$\frac{<3.0}{<3.0}$	
	AVG		10700	959	101	977	$\overline{101}$	<3.0	<0.3
4/11	1	0807	11300	402	46	•		<3.0	
	2	1000	11300	344	40	657	76	<3.0	
	3	1240	<u>11500</u>	<u>331</u> 359	38 41			$\frac{<3.0}{<3.0}$	•
	AVG		11400	359	41	657	76	<3.0	<0.3
4/12	1	0807	11300	408	47			<3.0	
	2	1000	11400	144	17	787	91	<3.0	
	3	1240	11400	$\frac{179}{244}$	21_	-		$\frac{<3.0}{<3.0}$	
	AVG		11400	244	28	787	91	<3.0	<0.3

FOOTNOTES:

a - Time reported is when velocity profile begun

b - Lb/hr expressed as equivalents of SO_2

c - Lb/hr expressed as equivalents of NO_2 , all three NO_{\times} samples taken during Run 3.

d - Detection limit is 3ppm, averaged in as 3ppm

EXAMPLE CALCULATIONS

FLOW RATES

*Actual Cubic Feet per Minute (ACFM)

ACFM = Velocity x Stack Cross - Sectional Area

Example: Based on 4/8 averages -

ACFM =
$$56.5 \frac{\text{ft}}{\text{sec}} \times \frac{4.08(\text{ft})^2 \times 11}{4} \times \frac{60 \text{ sec}}{\text{min}}$$

ACFM = 44,300 ft³/min

•Dry standard cubic feet per minute (DSCFM) @ 60 °F and 29.92 in.Hg

DSCFM = ACFM x
$$\frac{\text{Barometric Pressure}}{\text{Standard Pressure}}$$
 x $\frac{\text{Standard Temp}}{\text{Stack Temp.}}$ x $\left(1-\frac{\text{mole}}{\text{fraction}}\right)$

Example: Based on 4/8 averages-

DSCFM = 44,300 (ACFM)
$$\times \frac{29.95(in.Hg)}{29.92(in.Hg)} \times \frac{520 (°R)}{1305 (°R)} \times (1-0.2660)$$

 $DSCFM = 13,900 \text{ ft}^3/\text{min}$

EMISSION RATES

•Emission Rates- SO₂, NO_x, H₂S, TRS (1b/hr)

Emission Rate = $\frac{\text{Concentration of Compound (ppm,dry)}}{10^6}$ x DSCFM x

Example: Based on 4/8 averages-

S0₂ Emission Rate =
$$\frac{8950 \text{ (ppm S02,dry)}}{10^6} \times 13,000 \text{ DSCFM } \times \frac{64 \text{ 1b S02}}{379 \text{ SCF}} \times \frac{60 \text{ min}}{10^6}$$

SO₂ Emission Rate = 1180 lb/hr

Note: H_2S and TRS Emission Rates are expressed as equivalent SO_2 ; NO_{\times} Emission Rate is expressed as NO_2 ; Total SO_2 Emission Rate is the sum of SO_2 and TRS Emission Rates

SULFUR PLANT EFFICIENCY

•Plant Efficiency =
$$\frac{\text{Sulfur Recovered}}{\text{Sulfur Recovered}} \times 100\%$$

where:

Sulfur recovered = liquid sulfur production (LTPD) Sulfur emitted = SO_2 + TRS Emission Rates (expressed as elemental sulfur) (LTPD)

Example: based on 4/8 averages-

Plant Efficiency =

$$\frac{144.7 \text{ LTPD}}{\text{144.7 (LTPD)}} + \frac{1180 + 138 - 1}{\text{hr}} \times \frac{32 \text{ lbs}}{64 \text{ lb SO}_2} \times \frac{\text{LT}}{2240 \text{ lb}} \times \frac{24 \text{ hr}}{\text{day}}$$

Plant Efficiency = 95.3%